Resolving the F_2 Bond Energy Discrepancy Using Coincidence Ion Pair Production (cipp) Spectroscopy.

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During coincidence ion pair production (cipp) measurements a signal is recorded only when anions and cations are produced simultaneously. The coincident ion production ($F^+ + F^-$) measured in this study is formed via one-photon excitation to bound high energy Rydberg states, followed by state crossing to ion-pair states above the dissociation limit and subsequent dissociation to form F^+ and F^- ions. This mechanism can be presented as:

$F_2 + h\nu \longrightarrow F_2^{**}$	One-photon excitation
$F_2^{**} \longrightarrow F^+F^-$	Rydberg ⟶ ion-pair state crossing
$F^+F^- \longrightarrow F^+ + F^-$	Ion pair dissociation

Cipp spectra of F_2 were recorded on the DELICIOUS III coincidence spectrometer[1] in the one-photon excitation region of 125 975–126 210 cm^{-1}. The $F^+ + F^-$ signal in this frequency range shows rotational band head structure, corresponding to F_2 Rydberg states crossing over to the ion pair production surface.

Through a simulation of the spectra and quantum defect analysis, five Rydberg states spectra were characterized and assigned, four $^1\Sigma_u$ states and one $^1\Pi_u$ state. (**Figure 1**.).

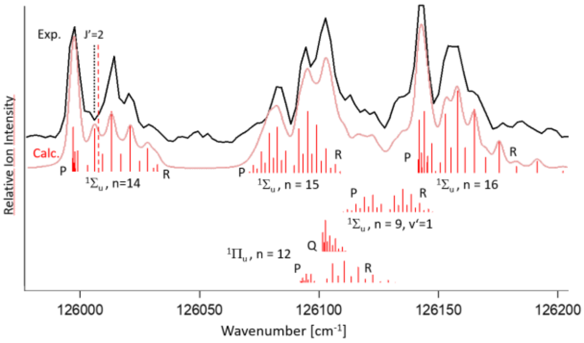

Fig. 1. F_2 coincidence ion pair production spectra in the 125 950 – 126 210 cm^{-1} photon energy region. Experimental spectrum (black, top), calculated spectrum (red, middle) using 5 cm^{-1} linewidths, and rotational lines (red sticks, bottom). The ion pair threshold is indicated by a red dashed line. J'=2 for the $^1\Sigma_u^+[3/2]14p\pi_u$ state is indicated by a dashed black line.. Assignments for the spectral contributions are indicated

As can be seen from the figure some of the assigned states overlap each other. This makes accurate determination of the spectroscopic constants somewhat problematic, resulting in large error bars. The spectroscopic parameters derived from the simulation are listed in **Table 1.**

Table 1. Rydberg state specifications ($Ry\ ^{2\Sigma+1}X[\Omega_c]n l\lambda$ for $^{2\Sigma+1}X$ = term symbol for the Rydberg state) vibrational quantum numbers (v´), band origin (ν^0) and rotational parameters ($B´$, $D´$) based on simulation shown in Fig. 1 and quantum defect analysis.

State assignments	v´	Band origin (ν^0) [cm^{-1}]	B_e'^{a} [cm^{-1}]	D_e´^{a} [cm^{-1}]
$^1\Sigma_u^+[3/2]14p\pi_u$	0	125 999	1.18 ± 0.01	0.0015± 0.0003
$^1\Sigma_u^+[3/2]15p\pi_u$	0	126 086	0.9 ± 0.1	(0)
$^1\Pi_u[1/2]12p\sigma_u$	0	126 099	1 ± 0.1	(0.0002)
$^1\Sigma_u^+[3/2]9p\pi_u$	1	126 126	0.9 ± 0.1	(0)
$^1\Sigma_u^+[3/2]16p\pi_u$	0	126 147	0.96 ± 0.1	(-0.0014)

[a] Precision of parameters is affected by overlap of spectra and rotational line overlaps.

One of the key features of the simulation is the apparent lack of the $J' = 2$ rotational peak in the first sigma state of the experimental spectrum (at around 126 000 cm^{-1}). This peak, which should occur at 126 005 cm^{-1} (see Fig. 2) must be missing because its excited state energy level is below the ion pair production threshold.

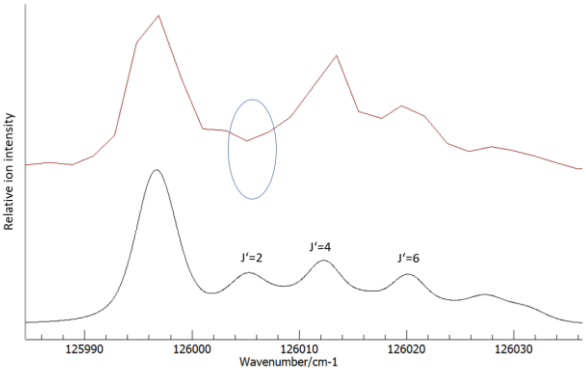

Fig. 2. Comparison of simulation to experimental data showing clear lack of the J'=2 rotational peak belonging to the $^1\Sigma_u$(n=14, v'=0) state.

This finding allows us to estimate, with high certainty, the $F_2 \longrightarrow F^+ + F^-$ dissociation threshold, which can also be used to determine the F–F bond dissociation energy, $D_0(F_2)$. The energies (E) of the rotational levels $J' = 2$ and $J' = 3$ of the $^1\Sigma_u^+ 14p\pi_u$ state, converging to the $^2\Pi_g[3/2]$ ground state of F_2^+ are,

$$E\,(^1\Sigma_u^+[3/2]\ 14p\pi_u\,(v' = 0, J' = 2)) = 126\,004\ \text{cm}^{-1} = 15.6225\ \text{eV}$$

$$E\,(^1\Sigma_u^+[3/2]\ 14p\pi_u\,(v' = 0, J' = 3)) = 126\,011\ \text{cm}^{-1} = 15.6234\ \text{eV}$$

This means that the ion pair production threshold energy for $F_2 \longrightarrow F^+ + F^-$ can be given as $15.6229_4 \pm 0.0004_3$ eV. Using the F adiabatic ionization energy of 17.42283 ± 0.00005 eV[2] and its electron affinity of 3.401190 ± 0.000002 eV[2] this translates to the following $D_0(F_2)$ value:

$$D_0(F_2) = 15.62294\ \text{eV} - 17.42283\ \text{eV} + 3.40119\ \text{eV} = 1.6012_9 \pm 0.0004_4\ \text{eV}$$

This value was further independently confirmed by photoelectron photoion coincidence (PEPICO) experiments which gave the 0 K appearance energy of 19.0242 ± 0.0006 eV for $F_2 \longrightarrow F^+ + F + e^-$, which translates to the following $D_0(F_2)$ value

$$D_0(F_2) = 19.0242\ \text{eV} - 17.42283\ \text{eV} = 1.6013_2 \pm 0.0006_2\ \text{eV}$$

These two experiment results can then be combined to find a weighted average **F_2 dissociation energy of $1.6013_0 \pm 0.0003_6$ eV** which is in good agreement to previous ATcT values and improves its accuracy by more than a factor of two.

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